

# Origin of water in the inner Solar System: A kinetic Monte Carlo study of water adsorption on forsterite

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## ABSTRACT

The origin of water in the inner Solar System is not well understood. It is believed that temperatures were too high in the accretion disk in the region of the terrestrial planets for hydrous phases to be thermodynamically stable. Suggested sources of water include direct adsorption of hydrogen from the nebula into magma oceans after the terrestrial planets formed, and delivery of asteroidal or cometary material from beyond the zone of the terrestrial planets. We explore a new idea, direct adsorption of water onto grains prior to planetary accretion. This hypothesis is motivated by the observation that the accretion disk from which our planetary system formed was composed of solid grains bathed in a gas dominated by hydrogen, helium, and oxygen. Some of that hydrogen and oxygen combined to make water vapor. We examine quantitatively adsorption of water onto grains in the inner Solar System accretion disk by exploring the adsorption dynamics of water molecules onto forsterite surfaces via kinetic Monte Carlo simulations. We conclude that many Earth oceans of water could be adsorbed.

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## 1. Introduction

Water is ubiquitous in the inner Solar System. Earth demonstrably has water, as does Mars (Baker et al., 1991; Carr, 1996; Boynton et al., 2002). The D/H ratio of Venus is about 100 times that of Earth's oceans (Donahue et al., 1983), suggesting that Venus preferentially lost H relative to D through UV photodissociation of H<sub>2</sub>O at the top of the Venus atmosphere. Mercury and the Moon appear to be bone dry, possibly due to volatile loss in giant impacts (Taylor, 2001). Asteroids appear to contain both hydrous and anhydrous examples, with the hydrous examples being concentrated towards the outer part of the Main Belt (Grady et al., 1989).

There is, however, no consensus on the origin of water in the terrestrial planets. Suggested sources of water include direct adsorption of hydrogen from the nebula into magma oceans after the planets formed, and delivery by comets, hydrous asteroids, or phyllosilicates migrating from the asteroid belt, and hydrous minerals forming in the inner Solar System and accreting directly to the terrestrial planets.

We discuss each of these hypotheses below. We then explore the possibility of direct adsorption of water vapor onto grains in the accretion disk. After all, silicate grains were bathed in a gas of hydrogen, helium, and oxygen, and some of that hydrogen and

oxygen combined to make water vapor (Drake, 2005; Stimpfl et al., 2006). We will explore this hypothesis using kinetic Monte Carlo simulations of the adsorption of water on to forsterite grains.

## 2. Sources of water

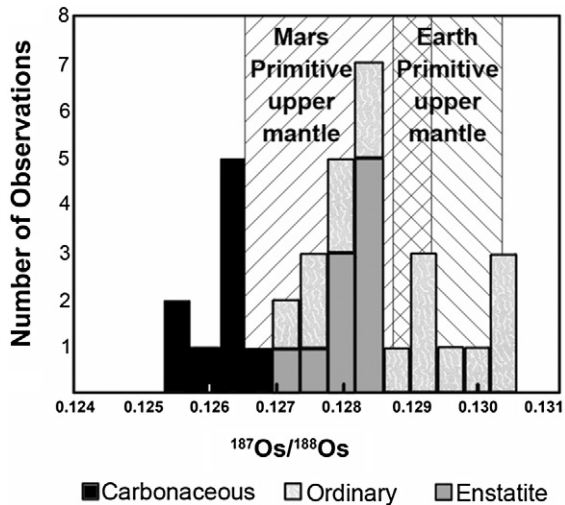
The origin of water in the terrestrial planets is intimately related to physical conditions in the accretion disk. It is generally held that temperatures were too high in the inner Solar System for hydrous phases to exist in the accretion disk, so the terrestrial planets accreted "dry" (Boss, 1998). Water was delivered from exogenous sources (e.g., direct adsorption of molecular hydrogen from the nebula, and from comets and meteorites). We will briefly discuss each of these theories. Then we will investigate the possibility that the accretion disk was hot as postulated by Boss (1998) and that water was adsorbed directly from the gas in the accretion disk onto grains. Generally discounted is that the accretion disk was cooler than postulated by Boss (1998) and that the terrestrial planets directly accreted hydrous silicate phases. This idea will not be discussed further.

### 2.1. Water from hydrogen in the accretion disk

Sasaki (1990) and Ikoma and Genda (2006) have suggested that water arrived at Earth by direct adsorption of hydrogen from nebular gas into a magma ocean after Earth formed. Water is formed

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**Fig. 1.**  $^{187}\text{Os}/^{188}\text{Os}$  ratios in carbonaceous, ordinary, and enstatite chondrites, and in the Earth's primitive upper mantle and Mars' primitive upper mantle. Earth's primitive upper mantle is distinct from water-bearing carbonaceous chondrites. Mars primitive upper mantle is the authors' estimate based on conversations with A. Brandon (personal communication, March, 2008). Earlier estimates of the martian mantle were probably compromised by incomplete dissolution of sample (A. Brandon, R. Walker, personal communications, March, 2008).

by reaction of  $\text{H}_2$  with  $\text{FeO}$  in the magma ocean. This reaction is reducing, i.e., the magma ocean would be reduced relative to its initial state. In fact the upper mantle of Earth is approximately three orders of magnitude more oxidized than would be expected for equilibrium between metal and silicate. Thus direct adsorption of molecular hydrogen from the nebula is not consistent with the current oxidation state of the Earth.

## 2.2. Water from comets

Comets capable of delivering water to Earth are believed to have formed in the region beyond Uranus in the outer Solar System (Morbidelli et al., 2000), where temperatures were below 70 K (Yamamoto, 1985). It is possible to predict isotopic, elemental and molecular ratios in ices formed at these temperatures. The  $\text{H}_2\text{O}/^{130}\text{Xe}$  ratio in the Earth and the inventories of H, C, and N all point to a negligible ( $10^{-4}$ ) contribution from comets to the water budget of Earth (Dauphas, 2003). Measurements of D/H ratios and Ar/ $\text{H}_2\text{O}$  or Ar/O ratios in comets also lead to the conclusion of a negligible contribution to Earth's water budget by comets (Drake, 2005; Stimpfl et al., 2006).

## 2.3. Water from asteroids

Hydrated asteroids have been postulated as a source of Earth's water. Morbidelli et al. (2000) have shown that a small fraction of asteroidal material from the Main Belt accreted to Earth. The delivery of water from asteroids can be examined by looking at the Os (Fig. 1) and D/H (Fig. 2) isotopic signatures of the Earth. Only carbonaceous chondrites contain significant amounts of water (Fig. 2). Os isotopes in Earth are quite unlike any hydrous carbonaceous chondrite meteorite falling to Earth today. Os isotopes in Earth's primitive upper mantle have an anhydrous ordinary chondritic signature. It has been suggested that mixtures of anhydrous ordinary chondrites and hydrous carbonaceous chondrites could yield an appropriate Os isotopic signature for Earth. This hypothesis is certainly possible, but the same mixture would have to satisfy both  $^{187}\text{Os}/^{188}\text{Os}$  ratios and D/H ratios in Earth (Figs. 1 and 2).

## 2.4. Adsorption of water directly from the accretion disk

Drake (2005) proposed that adsorption of water molecules from the gas in the accretion disk directly on to grains prior to their accretion into planetesimals and, eventually, planets may be the source of some or all of the water present in Venus, Earth, and Mars 4.5 Ga ago. After all, silicate grains were bathed in a gas of hydrogen, helium, and oxygen, and some of that hydrogen and oxygen combined to make water vapor (Drake, 2005; Stimpfl et al., 2006). Olivine is abundant in interplanetary dust particles. Stimpfl et al. (2006) carried out preliminary calculations on adsorption of water on to forsterite (the Mg end member of the olivine solid solution series) grains and concluded that adsorption was indeed a potential source of water in the terrestrial planets. In this paper we build on the work of Drake (2005) and Stimpfl et al. (2006) using kinetic Monte Carlo (KMC) calculations to quantify the adsorption of water on to forsterite grains as a function of temperature. We conclude that many Earth oceans of water could have been adsorbed onto grains prior to the accretion of the terrestrial planets, accounting for some or all of the accreted water.

## 3. Water adsorption on forsterite

Fluid molecules can adsorb on to a solid surface either by physisorption or chemisorption. Physisorption is characterized by weak van der Waals forces and consequently low activation energies, while chemisorption involves strong chemical bonds between the substrate and the adsorbing molecules. Chemisorption includes associative adsorption where molecular water is adsorbed onto the surface by means of strong interactions between underbonded surface cations and the oxygen in the water molecule, and dissociative adsorption where the covalent bonds within the water molecule are broken and are substituted by covalent bonding between the  $-\text{OH}$  and  $-\text{H}$  water radical and the substrate. Initially, adsorption was not considered as a potential delivery source of water as it was thought that water molecules were weakly physisorbed on to the mineral surfaces. Later, de Leeuw et al. (2000a, 2000b) and Stimpfl et al. (2006) carried out theoretical calculations using energy minimization techniques and showed that molecular water was strongly chemisorbed onto forsterite surfaces. Note that the above energy minimization calculations were carried out at 0 K. To simulate conditions in the accretion disk prior to planetary formation, we must consider environmental conditions (pressure, temperature). To this end we carry out KMC simulations in tandem with the calculations of Stimpfl et al. (2006), both of which are described below.

### 3.1. Models and methods

We have used two complementary techniques to study the interaction of water with forsterite, namely energy minimization and kinetic Monte Carlo. Both are based on the description of the systems by interatomic potentials, where the interactions between all atoms are described by a collection of long-range Coulombic interactions and short-range forces, including attractive van der Waals interactions and short-range repulsions. Interatomic potential methods are appropriate for this type of investigation as they allow for the modeling of relative large simulation cells and hence dilute adsorption of the water at extensive surface areas. In addition, these methods have been shown to give excellent results for the quantitative calculation of adsorption geometries and energies that agree well with both experiment and quantum mechanical calculations (e.g., de Leeuw and Cooper, 2003).

#### 3.1.1. Interatomic potential model

We have used the potential parameters derived for silica by Sanders et al. (1984) and MgO by Lewis and Catlow (1985), in

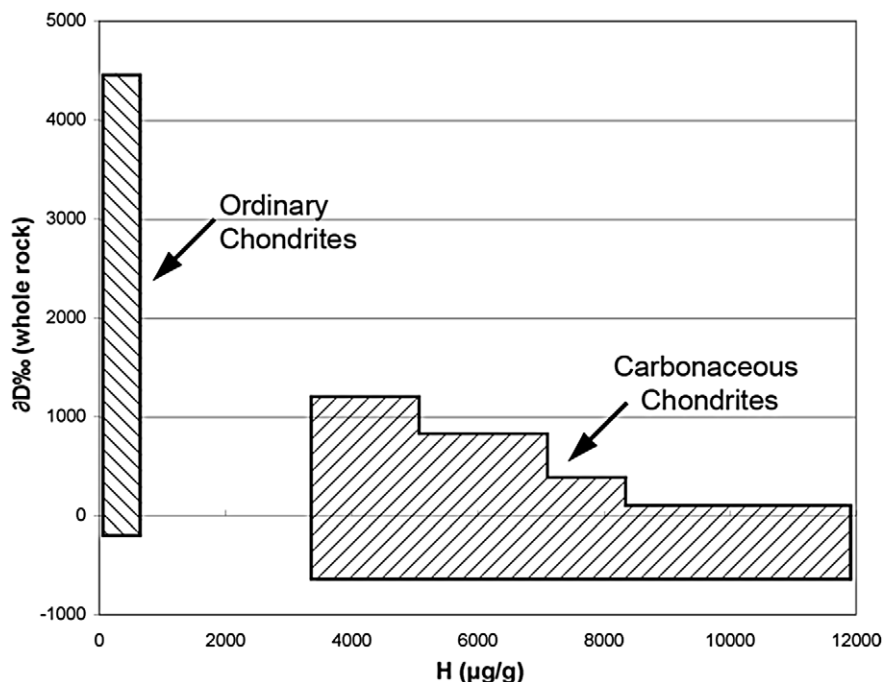


Fig. 2. Abundances of H versus  $\delta D$  for carbonaceous chondrites and ordinary chondrites. While a mixture of carbonaceous chondrites and ordinary chondrites could match the  $^{187}\text{Os}/^{188}\text{Os}$  ratios in the Earth's primitive upper mantle, that same mixture must also match  $\delta D = 0$  (i.e., VSMOW–Vienna Standard Mean Ocean Water). Data fields are derived from Zinner (1988).

combination with the potential model of de Leeuw and Parker (1998) for water. Although the  $\text{SiO}_2$  and  $\text{MgO}$  potential models were derived separately, they are fully compatible with each other and transferable to other systems, and the combination of both models to simulate  $\text{Mg-Si-O}$  systems has been carried out successfully in a number of previous studies (Wright and Catlow, 1994; Watson et al., 1997).

The water potential model was derived empirically from the properties of the water molecule, dimer and liquid and was further tested in simulations of a number of ice structures. The calculated energies of dimerization and condensation to liquid water are in excellent agreement with experiment, whereas the experimental structure of the liquid water, as shown by the radial distribution functions (RDFs), is also reproduced well by the simulations in terms of peak positions and heights (de Leeuw and Parker, 1998).

The interactions between the water and the mineral surfaces were obtained according to the method by Schröder et al. (1992) and they have been used in hydration studies of the surfaces of  $\text{MgO}$  (de Leeuw et al., 1996),  $\text{SiO}_2$  (de Leeuw et al., 1999; Du and de Leeuw, 2004) and forsterite itself (de Leeuw et al., 2000a, 2000b), giving adsorption energies in good agreement with directly comparable experimental techniques such as Temperature Programmed Desorption (Fubini et al., 1989) as well as first-principles Density Functional Theory (DFT) calculations (see Table 1).

### 3.1.2. Water adsorption-energy on forsterite surfaces: Energy minimization

Using the interatomic potential model described above, Stimpfl et al. (2006) mapped out the chemisorption (associative adsorption to be precise) energy landscape of water on various forsterite surfaces by probing the reactivity of individual surface adsorption sites using a single water molecule. Specifically, the chemisorption energy landscapes of the {010} and {100} surfaces of forsterite were quantified and reported in Stimpfl et al. (2006), while the results for the {110} surface are still unpublished (Stimpfl, personal communication). These three surfaces were initially chosen

Table 1

Comparison of interaction energies calculated from Density Functional Theory (DFT) and interatomic potential-based simulations for the adsorption of water at selected  $\text{MgO}$ ,  $\text{SiO}_2$  and  $\text{Mg}_2\text{SiO}_4$  surfaces.

Surface	Adsorption energies ( $\text{kJ mol}^{-1}$ ) DFT	Interatomic potentials
$\text{MgO}$ {001}	−40.5 <sup>a</sup>	−37.6 <sup>b</sup>
$\text{SiO}_2$ {0001}	−45.3 <sup>c</sup>	−56.9 <sup>c</sup>
$\text{Mg}_2\text{SiO}_4$ {010}	−119.8 <sup>d</sup>	−124.1 <sup>e</sup>

<sup>a</sup> Finocchi and Goniakowski (2001).

<sup>b</sup> de Leeuw et al. (1996).

<sup>c</sup> Du and de Leeuw (2004).

<sup>d</sup> This work.

<sup>e</sup> de Leeuw (2001).

because they span a wide range in stability, with the {010} surface being the most stable ( $1.28 \text{ J/m}^2$ ) and the {110} the least stable ( $3.18 \text{ J/m}^2$ ) (de Leeuw et al., 2000a). Therefore the surface environments for these three planes were thought to provide a variety of sorption sites with marked differences in heat of adsorption. It has to be noted that on the unstable {110} surface of forsterite, associative adsorption of the water molecule was followed by dissociation and incorporation of the water molecule in the surface as protons and hydroxy groups (de Leeuw et al., 2000a). In the computations of Stimpfl et al. (2006), the bulk crystal was initially cleaved along the {010} and {100} directions to yield the respective surfaces (slabs). Then, the different surfaces were relaxed using the appropriate potential, with periodic boundary conditions applied in the planes of the surfaces. Particular care was taken to ensure that the computed bond distances and angles converged to those of the bulk material at the center of the slabs; in other words, the thickness of the slabs was chosen in order to prevent surface relaxation effects being sensed at the center of the slabs. Each surface was then divided into a grid, with the grid spacing equaling  $0.25 \text{ \AA}$  along both directions respectively. Next, the water molecule was positioned at each grid point, and the total potential energy of the system ( $E_{s+w}$ , where  $s + w$  stands for surface + water molecule) was systematically obtained via energy-minimization as a function

of water molecule location. The in-plane coordinates of the water molecule were held fixed, while the orientation as well as the height of the water molecule was allowed to vary. From the knowledge of  $E_{s+w}$  the surface adsorption energy map ( $U$ ) was obtained as given in Eq. (1), where  $E_s$  is the energy of the slab, and  $E_{H_2O}$  represents the self-energy of the water molecule.

$$U = [E_{s+w} - (E_s + E_{H_2O})]. \quad (1)$$

### 3.1.3. Kinetic Monte Carlo (KMC) calculations

The evolution in time of any chemical system can be modeled by the atomistic KMC method. The KMC algorithm uses the probabilistic Monte Carlo procedure to numerically model the dynamically evolving chemical system; specifically, this method takes into account the fact that the time evolution of a chemical system is a discrete, stochastic process instead of a deterministic, continuous process. Thus, the KMC procedure accurately accounts for fluctuations and correlations inherent to the system under study and has been successful in modeling a wide variety of applications (Gillespie, 1977).

The success of the KMC procedure hinges upon the ability to generate the reaction rates of all possible chemical events that could occur in the system under study. Assuming that there are  $N$  possible chemical events possible, then the KMC procedure, based on a probability distribution function for reaction events (Gillespie, 1977) expresses the probability of occurrence of each event as follows:

$$P(r_i) = 1 - \exp(-R_i \delta t_i), \quad (2a)$$

where  $P_i$  represents the probability of occurrence of the  $i$ th event,  $r_i$  is a random number extracted from a uniform random number generator,  $R_i$  is its corresponding reaction rate, and  $\delta t_i$  is the time associated with the  $i$ th event. Based on Eq. (2a),  $\delta t_i$  is estimated stochastically as given in equation:

$$\delta t_i = -\frac{1}{R_i} \log(1 - r_i). \quad (2b)$$

Next only the event with the smallest  $\delta t$  is chosen to occur and the system is propagated for a time equaling the size of the smallest time step. The above steps are repeated and the system is propagated in time until it attains equilibrium as shown in Fig. 3.

In order to model the adsorption of water molecules onto forsterite surfaces (i) adsorption, (ii) desorption of water molecules (onto or from the mineral surface), and (iii) random-walk diffusion of water molecules in space are cataloged at every KMC time step. The temperature and pressure of the simulated system are chosen to represent the conditions corresponding to the accretion disk. The adsorption ( $R_{ads}$ ) and desorption ( $R_{des}$ ) rates are expressed via a Boltzmann distribution and given in equations:

$$\begin{aligned} R_{ads} &= \nu_a \exp(-E_{ads}/RT), \\ R_{des} &= \nu_d \exp(-E_{des}/RT), \end{aligned} \quad (3)$$

where the pre-exponents  $\nu_a$  and  $\nu_d$  are a measure of the probability of adsorption and desorption, respectively.  $E_{des}$  and  $E_{ads}$ , are the energies of desorption and adsorption, respectively. These equations and the simulation procedure are both described in greater detail in the following section.

### 3.2. Simulation procedure

In this work, we examine the associative adsorption kinetics, and ignore the dissociative process. Since dissociative energies are much larger in magnitude, any success with associative adsorption would only strengthen the possibility of adsorption as a delivery source of water in the inner Solar System. The {110} surface is a

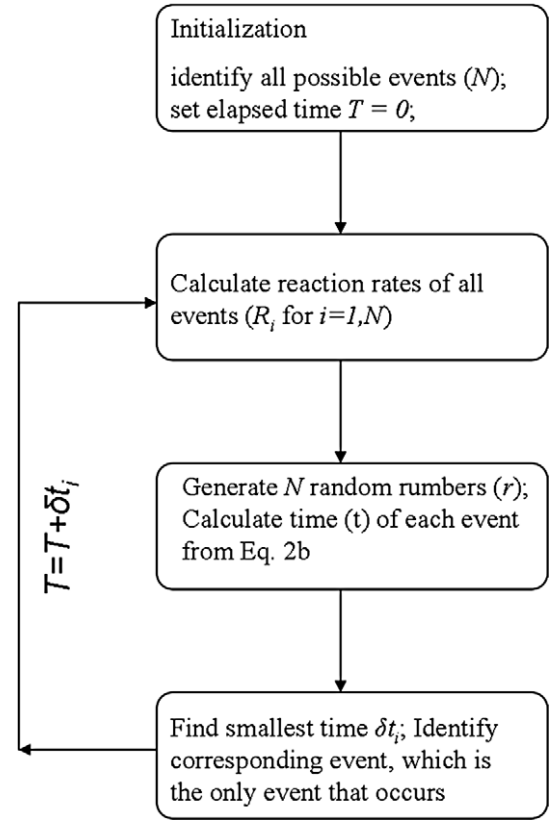


Fig. 3. Flowchart representing the workings of a KMC simulation.

highly reactive surface capable of supporting dissociation of the water molecule (de Leeuw et al., 2000a), and consequently we only investigate the {010} and {100} surfaces, whose average adsorption energies range from 106 kJ/mol ({010}) to 134 kJ/mol ({100}) (Stimpfl et al., 2006); Figs. 4a and 4b represent the energy distribution for the {100} and {010} surfaces, while Fig. 4c depicts the surface energy map of {100}.

If adsorption is a potential delivery source of water, then it is likely that it began at the initial stages of planet accretion, when dust and gas were still present at in the accretion disk, with the thermodynamic conditions during the initial stages characterized by partial pressures ( $P_{H_2O}$ ) of around  $10^{-8}$  bars (Lodders, 2003) and high temperatures (700–1400 K). In these simulations we allow only for monolayer coverage, because only the first water layer will form strong bonds with the surface, while any additional layer will interact with the substrate (i.e. water layer) only by means of low energy bonds (physisorption). Therefore, since we are interested in processes occurring at high temperature, it is reasonable not to consider multi-layer adsorption, as weakly adsorbed water molecules will be removed readily from the substrate at modest temperatures.

In order to mimic appropriate conditions, the simulation system is chosen to consist of the surface(s) placed in a suitable  $P$ - $T$  environment as shown in Fig. 5, where the three possible KMC events are depicted. At the start of each simulation, the slabs are initially water-free and the positions of the water molecules in space are assigned randomly (via a random number generator). Periodic boundary conditions are imposed in the  $X$ - $Y$  directions, to ensure that the total number of molecules is conserved. If any molecule is adsorbed on to the substrate, then a new molecule is introduced at  $Z_{max}$  (see Fig. 5), while if a molecule is desorbed, then the molecule further away from the substrate is ejected out of the simulation system.



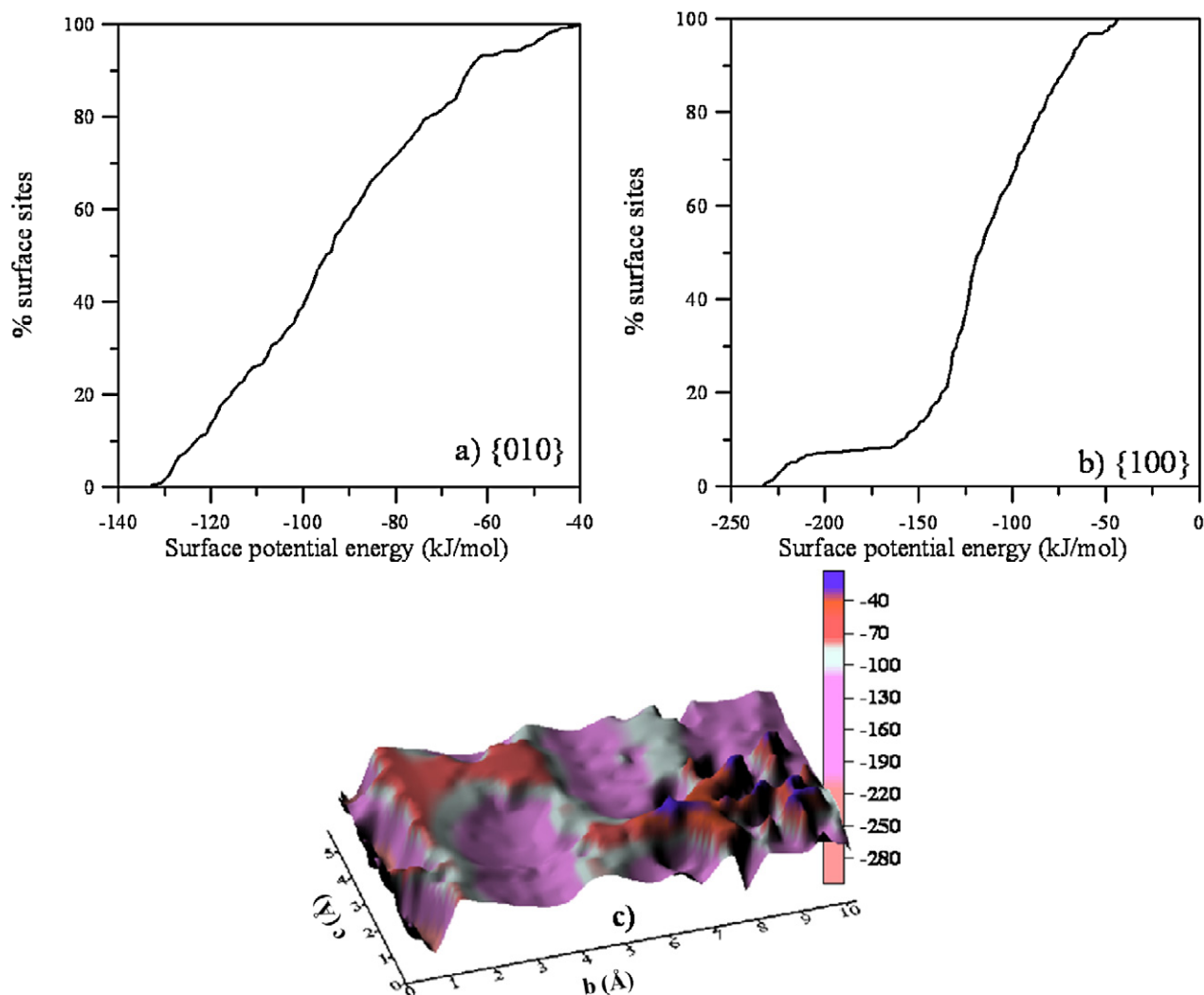


Fig. 4. (a and b) Energy distribution of the discretized {010} and {100} surfaces respectively; note that each surface site corresponds to an area of  $0.25 \text{ \AA} \times 0.25 \text{ \AA}$ . (c) Surface potential energy map for {100}; the energy units are in kJ/mol.

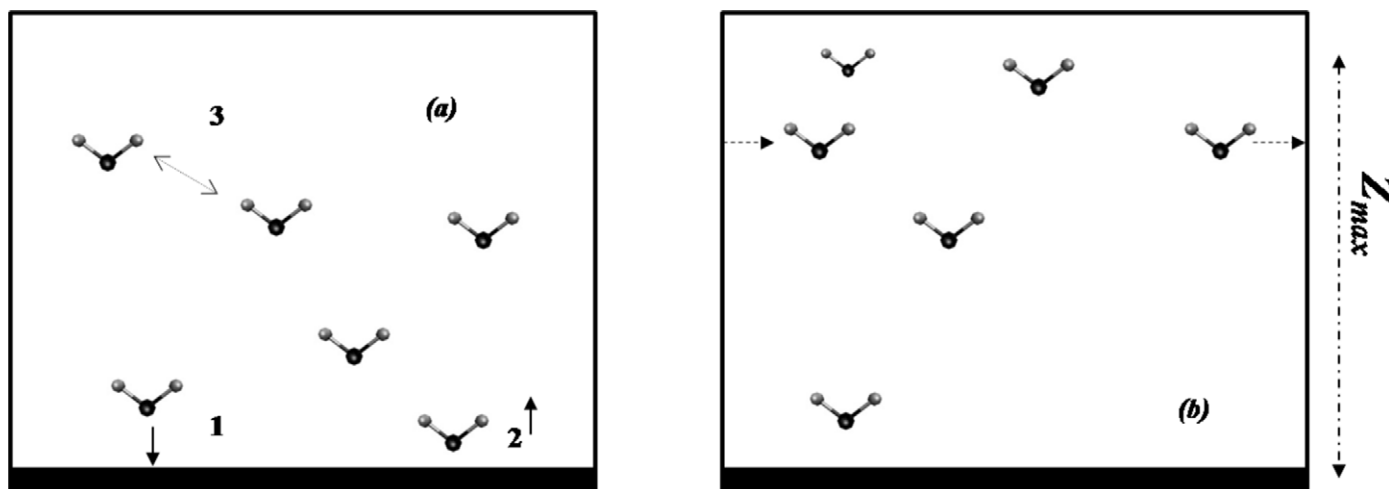


Fig. 5. (a) Illustration of three possible KMC events: 1 represents adsorption, 2 represents desorption and 3 represents diffusion; (b) 2-D illustration of the simulation system, where  $Z_{\text{max}}$  represents the system dimension perpendicular to the forsterite surface, and the arrows indicate the periodic boundaries applied to the system.

Any water molecule can adsorb, if the given site as well as neighboring sites (of the given site) that are within a cutoff radius equaling the typical hydrogen bond length ( $\sim 1.8 \text{ \AA}$ ), are unoccu-

piated. The molecule adsorbs with a rate  $R_{\text{ads}}$  that depends on two factors, namely the adsorption-site energy  $E_{\text{ads}}$ , and a frequency factor  $\nu_a$ , which is a function of (i) surface coverage (fraction of oc-

cupied adsorption sites)— $\theta_a$  and (ii) a flux factor  $\varphi_w$ . Specifically,  $\nu_a$  is given by Eq. (4), in which the parameter  $\varphi_w$  is in turn defined in Eq. (5), where  $\phi_a$  represents the frequency of collisions of water molecules on to the substrate, and  $P_{\text{H}_2\text{O}}$  equals the partial pressure of water-gas:

$$\nu_a = (1 - \theta_a)\varphi_w, \quad (4)$$

$$\varphi_w = P_{\text{H}_2\text{O}}\phi_a. \quad (5)$$

At every KMC step, the rates of desorption  $R_{\text{des}}$  of all adsorbed molecules are determined according to Eq. (3). We set  $E_{\text{des}}$  to equal  $-E_{\text{ads}}$ , since we are only considering associative adsorption/desorption processes (unlike dissociative processes where we need to account for intermediate states).  $\nu_d$  is a measure of the probability of the molecule to ‘escape’ from the adsorption site and is related to product of the frequency of vibration of the water molecule (inverse of the residence time) on forsterite surfaces ( $\eta_v$ ) and  $\theta_a$ .

If one neglects the presence of other elements and molecules in the accretion disk gas, and only consider the very small number-density of water-gas molecules as characterized by the low partial pressures of water, then ideal-gas conditions can be considered, and one can assume a ‘random-walk’ procedure to represent diffusion of water molecules in space. In order to calculate a ‘diffusion rate’ for the water molecules associated with the random walk process, the mean free path ( $\lambda_f$ ) and a corresponding ‘collision’ time ( $t_d$ ) is initially calculated for the given  $P$ - $T$  conditions; at every KMC step, if any of the desorption or adsorption times are smaller than  $t_d$ , the corresponding event is chosen to occur, and all molecules are diffused for a distance equaling the product of  $r_{(1\dots n)}$  and  $d_t$ , where  $r_{(1\dots n)}$  are a set of random numbers between  $-1$  and  $1$  and  $d_t$  is a diffusion distance corresponding to the chosen event time. If none of the adsorption and desorption times are smaller than  $t_d$ , the only event to occur is the diffusion of all molecules, with the respective diffusion distances equaling the product of  $r_{(1\dots n)}$  and  $\lambda_f$ .

#### 4. Results and discussions

In this section, we discuss the results obtained from KMC simulations carried out to examine surface adsorption as a possible source of water in the inner Solar System, using the steps enumerated in the previous section. The simulation system(s) which consisted of forsterite slabs encapsulated within a low-density water-gas environment, were investigated at temperatures between 700 and 1200 K, in steps of 100 K. The surface areas of the {100} and {010} slabs equaled 245.36 and 114.52  $\text{\AA}^2$  with the number of corresponding surface adsorption sites equaling 3924 and 1836, respectively. These slabs were obtained by periodically replicating the minimum-energy unit-cell configurations of the two surfaces as obtained by Stimpfl et al. (2006).

Assuming ideal-gas conditions,  $Z_{\text{max}}$  (length of the simulation system perpendicular to the substrate) was obtained from equation:

$$Z_{\text{max}} = Nk_B T / PA, \quad (6)$$

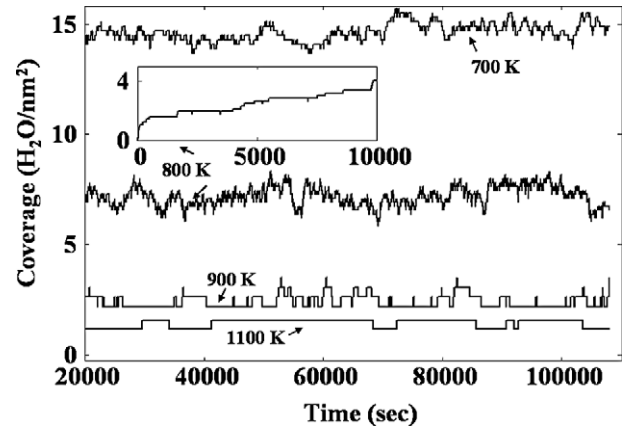
where  $k_B$  is the Boltzmann constant,  $N$  is the number of water molecules and  $A$  is the surface area of the forsterite slab. In all our simulations we set  $N = 10$ , resulting in, for example,  $Z_{\text{max}}$  to equal 56.2 m and 26.3 m at  $T = 1000$  K for the {100} and {010} surfaces respectively. Such large values of  $Z_{\text{max}}$  are required given the relatively comparable magnitude of  $\lambda_f$ , whose value along with other simulation parameters are listed in Table 2.

Fig. 6 depicts the variation in concentration of adsorbed water on to the {100} surface at the various temperatures. Fig. 6 shows that, during the initial stages (see inset), there is a gradual increase

**Table 2**

List of all simulation parameters used in the KMC simulations;  $\lambda_f$  and  $t_d$  represent the mean free path and collision time of a diffusing water molecule,  $\phi_a$  represents the frequency of collisions of water molecules on to the adsorbing mineral surface,  $\eta_v$  is the measure of the frequency of vibration of a water molecule on the mineral surface,  $P_{\text{H}_2\text{O}}$  is the partial pressure of water in space and  $N$  is the number of water molecules diffusing in space.

$\lambda_f$	$t_d$	$\phi_a$	$\eta_v$	$P_{\text{H}_2\text{O}}$	$N$
34 mm	$1.08 \times 10^{-3}$ s	$5 \times 10^{-10}$ (s Pa) $^{-1}$	$1.1 \times 10^{13}$ Hz	$10^{-3}$ Pa	10



**Fig. 6.** Variation in equilibrium surface coverage of the {100} surface at different temperatures as a function of time. Note that equilibrium surface coverage is achieved at all temperatures in less than 20,000 s ( $\sim 5$  h), vastly shorter than accretional timescales of tens of millions of years. The inset figure represents the initial variation in surface coverage of the {100} surface at 800 K before equilibrium is attained.

in the adsorbed water concentration (or surface coverage), until *equilibrium* (at the respective temperatures) is attained. The attainment of equilibrium suggests that *water is retained on the surfaces even at high temperatures, implying that adsorption of gaseous water onto dust grains can start at the earliest stages of accretion.*

For better statistics, five different simulations were performed at each temperature, and the net surface coverage as a function of temperature was obtained by averaging over the equilibrium values obtained as shown in Fig. 7. The surface coverage vs temperature plot (Fig. 7) in conjunction with Fig. 6, readily points out two facts: (i) the time-scale to attain equilibrium (thousands of hours) is much smaller than time-scales usually associated with planet accretion (millions of years); and, more importantly, (ii) an exponential-like temperature dependence dictates the amount of surface-coverage. The much smaller molecular coverage at the higher temperatures can be attributed to the larger kinetic energies of the adsorbed water molecules at higher temperatures, which increases the ability of molecules to desorb from the forsterite surface.

Similar simulations were performed for the {010} surface, and the resultant surface coverages were much smaller as compared to the {100} surfaces at every corresponding temperature. In fact, at and above 800 K, there was negligible surface coverage, while at 700 K, the surface coverage was  $\sim 1$   $\text{H}_2\text{O}/\text{nm}^2$ . The enormous difference in surface coverage characteristics is a direct consequence of the fact that the {100} surface is much more reactive towards water adsorption (see Figs. 4a and 4b and Stimpfl et al., 2006).

Using the surface coverage data in conjunction with the knowledge of the Earth’s mass ( $\sim 6 \times 10^{24}$  kg), the mass of oceans, and an average grain size of 0.1  $\mu\text{m}$ , one can then approximately estimate the amount of adsorbed water onto Earth. However, to quantify the amount of water that could be stored in olivine grains one needs to know the habit of such minerals in the nebula during accretion. Wurm and Blum (1998) showed that early aggregates form by ac-

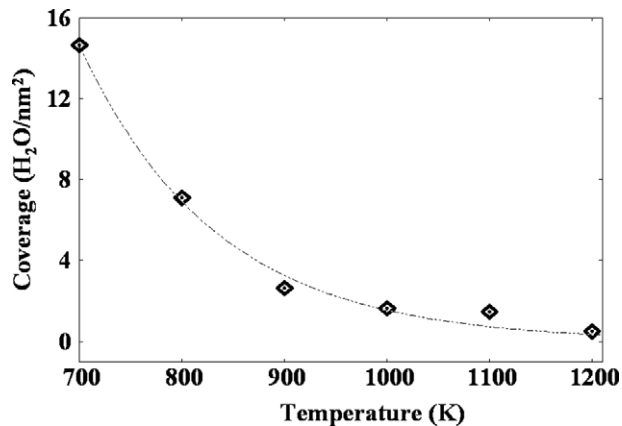


Fig. 7. Variation of equilibrium surface coverage of the {100} surface as a function of temperature.

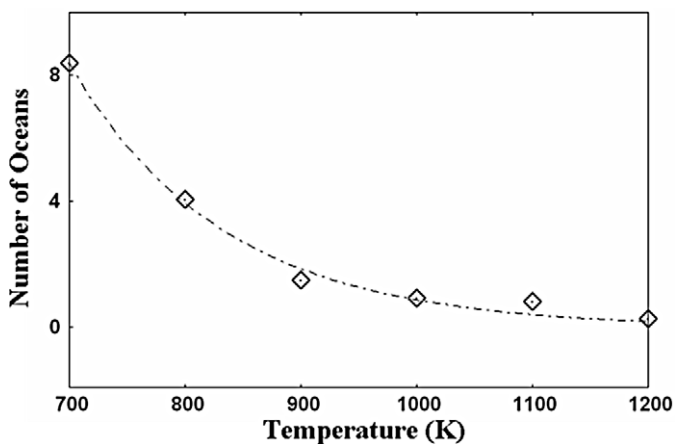


Fig. 8. Variation in the amount of adsorbed water expressed in terms of Earth oceans at different temperatures for a {100} surface coverage = 44%. Because of our conservative assumptions, these values constitute lower limits.

cretion of spherical grains which form fractal, chain like structures and similar morphologies have been observed in interplanetary dust particles as well. While other habits have been observed (see for example Bradley et al., 1983), for the sake of simplicity we will assume that all olivine grains were initially spherical. Assuming that a percentage of the dust particle's total surface area consists of {100} surface grains, the data pertaining to Fig. 7 can be readily expressed in terms of Earth oceans. Since the {100} surface constitutes about 44% of the surface area of a perfect forsterite crystal, Fig. 7 is re-expressed in terms of Earth oceans in Fig. 8 for a {100} surface percentage of 44%. From Fig. 8 is clear that adsorption is an important player in bringing water to the inner Solar System, and is responsible, at least in part for the Earth's water budget.

In the above simulations and consequent calculations, some important aspects were not taken into account for the sake of computational simplicity. For example, we allowed for the adsorption of only one water monolayer, while neglecting both surface and bulk diffusion. Furthermore, the fractal nature of the dust grains was not considered, meaning that the available surface area for adsorption would be much more than what was taken into account in our studies; we considered only fully crystalline and defect-free surfaces, meaning that stronger interactions with the water molecules would ensue if the material were (partially) amorphous (less stable) and/or had defects at the surface. Also, as pointed out earlier, the energetically stronger dissociative adsorption process was not considered. These factors, if included, would contribute positively towards more water adsorption/incorporation into the grains.

On the other hand, the effects of other elements and molecules in the accretion disk gas on the kinetics of water adsorption were not included. Specifically, H<sub>2</sub> molecules have a much higher concentration (~1000 times of H<sub>2</sub>O concentration) in the gas thereby implying a greater probability of H<sub>2</sub> occupying adsorbing sites as compared to H<sub>2</sub>O due to their relatively large flux on the adsorbing surface. However, the adsorption energies or equivalently the chemical-bonds of H<sub>2</sub>O with the forsterite surfaces are much stronger, which at the elevated temperatures addressed in this work, will lead to preferential desorption of H<sub>2</sub>. Future work will involve quantitative predictions of the effect of nebular species such as H<sub>2</sub> on the kinetics of adsorption of water on to forsterite. Since deuterated water was not considered in this study, future work will explicitly account for this and examine the reasons behind the differences in the D/H ratios of water on Earth (VSMOW) and accretion disk water. Further, we will also examine if adsorption could be a likely delivery mechanism for carbon and nitrogen to Earth. Finally, the presence of anhydrous meteorites when viewed in the context of the current study implies that there could be accretion and post-accretion processes that could have resulted in the complete loss of water from some meteorites. Such processes should be explored and accounted for in future sophisticated models examining adsorption of water.

## 5. Conclusions

We have examined adsorption of water on the surfaces of accretion disk dust grains as a possible source of water in the inner Solar System. Towards this end, we have used atomistic computational techniques to predict and quantify the amount of water that could possibly adsorb onto forsterite grains, a primary constituent of silicates in the accretion disk. Our results show that adsorption can bring a substantial amount of water to planets growing in the inner Solar System.

In this work, many assumptions have been made; we have assumed only a monolayer of water would be adsorbed on high energy sites; we have ignored bulk diffusion of water into the grains; and we have ignored the far more energetically favorable dissociative adsorption process. Perhaps most importantly, we have ignored the fractal nature of cosmic dust grains and the presence of surface defects. Fractal surfaces vastly increase the number of energetically available sites for adsorption. However, we have also ignored the effect of other accretion disk gas species on the kinetics of water adsorption. Thus our work provides a conservative lower limit of the amount of water that can be adsorbed onto grains prior to accretion.

Future work will involve more sophisticated models that account for all of these features. In addition, we must evaluate the effect of the D/H ratio of the adsorbed water. Finally, we must evaluate how much water is retained during accretion of the terrestrial planets. An early attempt at elucidating this problem is reported by Canup and Pierazzo (2006).

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